



Research paper

Physical properties and Na-activation of Egyptian bentonitic clays for appraisal of industrial applications

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ABSTRACT

Selected physical properties of bentonitic clays in the north Western Desert, Egypt were investigated to assess their potential use in industrial applications. Assessment tests included specific surface area (SSA), swelling index (SI), green (GCS) and dry (DCS) compressive strengths, rheological properties, and filtrate volume. The impact of Na-activation on swelling index and rheological properties was also considered. SSA, SI after Na-activation, GCS, and rheological properties were highly correlated with smectite content and a modified AgTU-CEC. Mineral impurities greatly influenced the physical properties. Quartz and feldspars reduced the rheological properties and increased the water loss. Halite and colloidal iron oxides increased swelling index and enhanced rheological properties. DCS was greatly influenced by the percentage of added water and kaolinite abundance. Na-activation improved the swelling index and rheological properties of halite-poor samples. The swelling index of Na-activated samples was a useful tool for determining the quality and grade of bentonitic clays. The suitability of the Egyptian bentonitic clays for drilling mud and bonding of foundry sands was determined by comparing the results with a standard bentonite and published industrial specifications. Egyptian bentonitic clays showed comparable compressive strengths with Wyoming Na-bentonite (SWy-1) by adding 8 and 10 wt.% clay to sand molds and can be used for most metal-type castings. Egyptian bentonitic clays with a high swelling index and low quartz and feldspar content, produced comparable rheological properties with the Wyoming Na-bentonite and met international drilling mud specifications. However, the filtrate volume measurements indicated that the samples require additional modifications to reduce water loss. Many desirable bentonitic clay properties were reduced by large quantities of kaolinite.

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1. Introduction

Assessment is a critical stage in the development or exploitation of bentonitic clay deposits (Harvey and Lagaly, 2013). Once a potential deposit has been identified, its physical and chemical properties have to be determined. Assessment involves laboratory tests of general properties and specific tests related to intended uses. Assessment also involves geologic, mineralogic and petrographic investigations. The geologic origin (Galán and Ferrell, 2013) of the clay has a major impact on its physiochemical characteristics. Clays are used by the industry in bulk form without significant beneficiation or after various physical or chemical processing techniques (Pickering and Murray, 1994; Christidis et al., 1997; Pruett and Pickering, 2006; Murray, 2007). Recently, special attention was directed to the applications of high quality clay minerals in the formulation of clay-polymer nanocomposites (CPN) (Bergaya

and Lagaly, 2007; de Paiva et al., 2008). The complexities of clay mineral science and some of the relationships among assessment variables have been detailed in the *Handbook of Clay Mineralogy* (Bergaya and Lagaly, 2013a, 2013b).

Today bentonite is an essential raw material in metal and oil production as well as numerous applications of the raw or processed forms for pet litter, waterproofing, sealing, animal feed, fillers, fertilizers, extenders, filtering, catalysts, clarifying, and decolorizing. The “best-use” of bentonite for increasingly complicated and diverse applications depends on an understanding of clay mineral structures, chemical compositions, and physical properties (Eisenhour and Brown, 2009). Several protocols for assessment involve simple and/or complicated test procedures; color, grain size distribution, purity, methylene blue absorption, surface area, Atteberg limits, cation exchange capacity, exchangeable cations, thermal analysis, viscosity and swelling, electron beam microscopy, compactability, compressive strength, chemical composition, and mineral content by XRD or infrared spectroscopy (Inglethorpe et al., 1993). Unique physico-chemical characteristics of bentonites such as sub-micrometer particle size, high cation exchange capacity (CEC),

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large surface area (up to 800 m²/g), and variable chemical composition (Eisenhour and Brown, 2009; Güven, 2009) were frequently related to smectite content (i.e. grade).

Assessment tests may be general or specific related to a particular application. For bentonite and other industrial clays, three distinct stages of laboratory assessment are suggested (Christidis, 2011): (i) identification of the clay minerals and associated minerals; (ii) determination of important physical and chemical properties of the clays; and (iii) comparison with standards. The first stage is useful to assess “grade” of bentonite based on smectite content. The second stage can evaluate “quality”; a measure of industrial performance that is related to physico-chemical properties (Inglethorpe et al., 1993). Many industrial associations have established standards for specific categories of use.

Kaolinite- and smectite-rich clay deposits of variable age occur widely within the Nile valley and delta, and the Western and Eastern Deserts of Egypt. Clay deposits with bentonitic characteristics have a long history of use extending, in Egypt, from the time of the Pharaohs to now. Many are used in the production of ceramics, including refractories, white ware, heavy clay products, and Portland cement. Clays in the Fayoum and Alamine areas with swelling characteristics were assessed recently for use in the production of lightweight aggregate (Ismail et al., 2014). Some of the clay deposits contain enough smectite to classify them as bentonitic clays or bentonites with potentially higher value usages.

Mineralogical variability in existing bentonitic clay quarries within the northern Western Desert of Egypt revealed differences that were correlated statistically with Province, age and quarry with a discriminant function analysis (DFA) (Agha et al., 2012). Differences in the mineral content were related to the paleo-weathering environment and sorting by detrital processes (Agha et al., 2013). The relatively low smectite content and high kaolinite content of all but one of the quarries justified their designation as bentonitic clays rather than purer smectitic bentonites derived from volcanic sources. Most of the samples lacked the high smectite content and chemical purity (Agha et al., 2012; Agha, 2015) contributing to the special properties of Na-bentonite from Wyoming.

The chief goal of this investigation was to answer the following questions: Do the physico-chemical characteristics and clay quality measures provided by laboratory assessment suggest ways that the industrial usage of the Egyptian clays might be expanded? What are the relationships between easily determined physical properties (specific surface area and swelling index) and mineralogical and chemical characteristics? Does Na-activation play a role in these relationships? Answers to these questions should be of benefit to the clay industry in Egypt and in other countries where similar clay deposits are located.

2. Methods and materials

Thirty one representative samples were selected for evaluation from 10 quarries in the north Western Desert collection used to support the earlier mineralogical and geological reports prepared by the authors (Agha et al., 2012, 2013). Approximate locations of the sample are summarized in Table 1. Quarry numbers are generally lower in the North. For more information on locations refer to Agha et al. (2013). Sample selection was based on composition and the availability of enough material to conduct assessment tests, including extractable cations, cation exchange capacity, specific surface area, swelling index, viscosity and binding strength. The CMS Na-bentonite Source Clay, SWy-1, was used as a comparison standard for physical properties related to industrial applications.

The whole-rock and clay mineralogy were reported in detail earlier (Agha et al., 2012). Mineral identification was carried out by matching observed d-values with those in MacDiff 4.2.5, and quantitatively

Table 1
Samples used in assessment tests, quarry location and stratigraphic age.

Quarry	Sample	Location	Name	Age
Q2	s007	South of Alamein city	Deir Abul Hegif	Middle Miocene
Q4	s021	South of El Hammam city	El Barkan	Lower Miocene
Q5	s029	Wadi El Natrun	Deir El Baramous	Upper Pliocene
Q6	s033	El Fayoum Depression	Qasr El Sagha	Upper Eocene
	s061			
Q7	s063		Kom Oshim	
Q8	s083		Girza	Middle Eocene
	s091			
Q9	s099		Qalamshah	
	s109			
Q10	s111		Cemetery	?
Q11	s113		Shaklofa	Middle Eocene
Q12	s119		Reigha	?

assessed with the whole-pattern, least-squares fitting method in CLAY++ (Ferrell, 2006; Ferrell and Dypvik, 2009).

A JEOL JSM 840A scanning electron microscope with energy dispersive X-Ray spectroscopy (SEM/EDX) was used to determine the elemental composition of individual grains of all bentonitic clay samples. Freshly broken samples (≤ 5 mm thick) were coated with gold and viewed perpendicular to bedding in the secondary electron imaging mode (SEI).

CEC and extractable Ca, Mg, Na, and K were determined with a variation of the AgTU method of Dohrmann (2006) that avoided the initial rinsing of the solids with distilled water. Extractable cations are those displaced from the clay by AgTU ion exchange as well as the dissolution of soluble minerals or evaporated pore solutions by the reagent solution. Two sample weights (15 and 30 mg) were used to identify the effects of partially soluble minerals on the extracted element quantities.

Specific surface area (SSA, area/mass of dry clay) determinations utilized the Ethylene Glycol Monoethyl Ether (EGME) method (Cerato and Lutenegeger, 2002). Thirty one samples were analyzed in 12 batches. For reliability, two replicates of each sample were measured. The quality control material, SWy-1, was employed for each batch of samples. The precision of this method yielded a coefficient of variation (CV) less than 0.1, or $CV = 10\%$, in accordance with Cerato and Lutenegeger (2002). SSA (m²/g) was calculated based on a K value (2.86×10^{-4} g) representing the weight of EGME that is required to form a monomolecular layer covering 1 m² of clay surface.

Thirteen samples representing a wide range of smectite and kaolinite contents were subsequently selected from the 31 used for SSA to measure swelling index, compressive strength, rheological properties, and filtrate volume. Swelling index (SI) was determined using the method of Inglethorpe et al. (1993) that compares the volume of 10 g of clay after water saturation to the original dry powder volume. Additional aliquots were Na-activated by 1, 2, 3, 4, 5, and 6 wt.% anhydrous sodium carbonate (analytical grade) and tested to determine the maximum swelling capacity (ratio of maximum swelling index of activated sample to raw material * 100).

Compressive strength was determined for wet (green compressive strength, GCS) and dry sand molds (dry compressive strength, DCS) to evaluate the suitability of the Egyptian clays for use as binders for molding sands in the foundry industry. The test specimen size and geometry were prepared in accordance with the American Foundrymen's Society (AFS) standard specification for the preparation of molding sand test samples as described in Ademoh (2008). Washed and screened (400–200 μ m) Quikrete Premium Play Sand No. 1113 was used for the molding sand. Percentage dry weight (Ps%) for the -400 μ m bentonitic clay additions were calculated according to Inglethorpe et al. (1993). Different percentages of clay (5, 8, and 10 wt.%) and moisture contents (2, 3, and 4 wt.%) were added to the sand and thoroughly mixed. Green sand molds (i.e. wet) were tested immediately after core preparation. Each sample was tested twice and the average result was reported. Dry

compressive specimen cores were oven-dried at 110 °C for an hour and left to cool in a desiccator before testing.

Important rheological test properties including apparent viscosity, plastic viscosity, yield point, and gel strength were determined. These drilling mud tests were performed in an 8-speed rotational direct-indicating viscometer; OFITE, Mod. 800 equipped with f0.2 torsion spring, using a method similar to American Petroleum Institute (API) Specification 13A (2010). The viscometer was calibrated by polydimethylsiloxane (132–80 Calibration Fluid, 100 cP). The speed accuracy was 0.1 rpm. Suspensions of raw bentonitic clays were prepared by adding 10.8 g, 22.4 g, and 30.4 g of dry bentonite to 350 ml of fresh water, representing suspension concentrations of 3, 6, and 8 wt.%, respectively. The rheological measurements were repeated for the 13 samples after activating them with their optimum Na₂CO₃% as indicated in the swelling test. The standard Na-Montmorillonite (not activated) was used as a control sample. The filtrate volumes produced by a standard suspension were determined in a filter press after 30 min at a pressure of 100 psi according to API 13A (2010).

Correlation and multiple regression analyses were used to explore the relationships among the physicochemical characteristics. The XRD and extractable cations data-frames were transformed (log-transformation) prior to the calculations because they were closed arrays (Aitchison, 1986) that sum to 100% (i.e. XRD minerals) or ratios to 100 g (i.e. extractable cations). The transformation should remove the effect of the closure problem from the data matrix (e.g. Barbera et al., 2009).

3. Results

3.1. Summary of mineralogical and AgTU extractable cation data from previous work (Agha et al., 2012; Agha, 2015)

Statistical summaries for the XRD-minerals, extractable cations, and AgTU-CEC results reveal a mean total smectite content of 44 wt.% (Table 2) and that median values for the cations are approximately the same for the two weight treatments except for Ca (Table 3). Kaolinite (sum of two varieties) and expandable smectite/illite (sum of four varieties) were the major groups of clay minerals in the Western Desert quarries. Total kaolinite wt.% varied from 14.6 to 57.7 and the total of smectitic clays (discrete and mixed-layered) ranged from 26.1 to 67.5 wt.%. The presence of halite and Fe-oxides in some samples was revealed by SEM/EDX. Sorting the values on the basis of increasing smectite content revealed a hint of a negative bivariate with kaolinite and the other mineralogical variables; quartz plus feldspar, illite, amorphous material, and calcite, but the structure of the bivariate was not rigorously evaluated.

The results of AgTU adsorption (AgTU-CEC) and cation displacement and dissolution (sum of extractable cations) were frequently almost twice as high for the cation sum compared to the AgTU-CEC (Table 3). For measurements based on 15 and 30 mg of sample, the effects of sample weight were only obvious in the extractable cation sums for four samples with calcite percentages equal to or higher than 2.5 wt.%. This was due to the dissolution of calcite during the preparation of the samples. The most notable characteristic of the data was the higher quantity

Table 3

Summary statistics for extractable cations and AgTU-cation exchange capacity obtained from 15 mg and 30 mg samples. All values in meq/100 g.

	AgTU-CEC 15	Na _{Ext} 15	Mg _{Ext} 15	Ca _{Ext} 15	K _{Ext} 15	ΣC _{Ext} 15
Maximum	106.5	100.9	27.6	150.1	4.7	260.9
Q3	73.1	66	21	101.7	2.6	166.6
Median	66.7	46.4	18.1	21.7	2.1	103.1
Q1	60.2	36.6	12.5	14.5	1.7	78
Minimum	53.5	19.9	5.1	2.6	1.3	47.3

	AgTU-CEC 30	Na _{Ext} 30	Mg _{Ext} 30	Ca _{Ext} 30	K _{Ext} 30	ΣC _{Ext} 30
Maximum	83.5	102.6	27.9	78.1	4.6	184.4
Q3	67.1	65.1	20.8	65.8	2.6	126.3
Median	62.2	46	17.8	21.3	2	102
Q1	56.3	36.1	12.1	14.3	1.6	76.7
Minimum	50.8	19.8	5.1	2.8	1.2	47.5

of extractable cations compared to AgTU-CEC. In some cases, extractable Na was also greater than AgTU-CEC due to the presence of halite.

3.2. Specific Surface Area (SSA)

The reliability of the SSA measurements for 12 batches of samples was evaluated statistically by a Shewhart control chart utilizing repeated measurements for SWy-1. All SWy-1 results (100%) were within the stable zone, exhibiting a relative standard error of 9.55%. SSA values for the duplicate samples (Fig. 1) varied from 202 to 458 m²/g, but typically ranged between 250 and 350 m²/g. Samples from Q4 (average = 440 m²/g), Q5 (average = 367 m²/g), and Q6 (average = 336 m²/g) were generally higher than the other quarries. The samples with relatively high SSA were usually expandable mineral-rich clays. All values of the untreated clays are lower than the 590 m²/g measured for SWy-1.

3.3. Swelling index and Na-activation

Swelling volumes of raw samples ranged between 34 to 82 ml gel/10 g with a median of 50 ml gel/10 g (Table 4). Three raw samples had a swelling index ≥ 60 ml gel/10 g; s029 (Q5), s111 (Q10), and s119 (Q12), while SWy-1 produced a swelling index of 96 ml gel/10 g. Two of the highest values (s029 and s119) were from halite-bearing samples, although these two samples were characterized by moderate to low grade.

After Na-activation, the SI increased and the maximum swelling capacity varied between 108% and 346%. The maximum SI for the activated samples was between 56 to 170 ml gel/10 g (shaded cells in Table 4). Four activated samples had swelling indices ≥ 100 ml gel/10 g (higher than the swelling index of SWy-1; s021 (Q4), s033 and s061 (Q6), and s111 (Q10). These samples were characterized by high smectite content and were halite-free. On the other hand, the halite-bearing samples showed the lowest values of maximum swelling index (less than 150%). The percentage of Na₂CO₃ that produced the maximum swelling differed from one sample to another. The majority exhibited their maximum swelling (completely activated and all the exchangeable cations replaced by sodium) with 1 wt.% to 2 wt.% Na₂CO₃, while the optimum Na₂CO₃ to activate s021 was 3 wt.%, and s083 required 6 wt.% Na₂CO₃.

3.4. Compressive strength

The summary statistics for compressive strengths of sand molds bonded by 5 wt.% bentonitic clay revealed minimal differences for GCS and large differences in DCS with increasing water content (Fig. 2A). The same general relationships applied for molds bonded by 8 wt.% and 10 wt.% clay. GCS values for SWy-1 (x – Fig. 2) were often equal to the maximum values produced by the samples. The Egyptian DCS median values of sand molds bonded by 8 wt.% and 10 wt.% clay were higher than the SWy-1 (Fig. 2B and C). Increased clay content produced

Table 2

Summary statistics for mineralogical data. Values in smectite and kaolinite columns represent the sums of species with varying SI layers or crystallite thicknesses reported in Agha et al., 2012. Qz = quartz; feld = feldspars.

Sample	Smectites	Kaolinites	Amorphous	Illite	Qz + feld	Calcite	Gypsum
Maximum	68	58	21	13	15	7	0
Q3	49	48	10	5	9	2	0
Median	44	35	7	4	6	0	0
Q1	36	28	6	2	3	0	0
Minimum	26	15	3	0	2	0	0

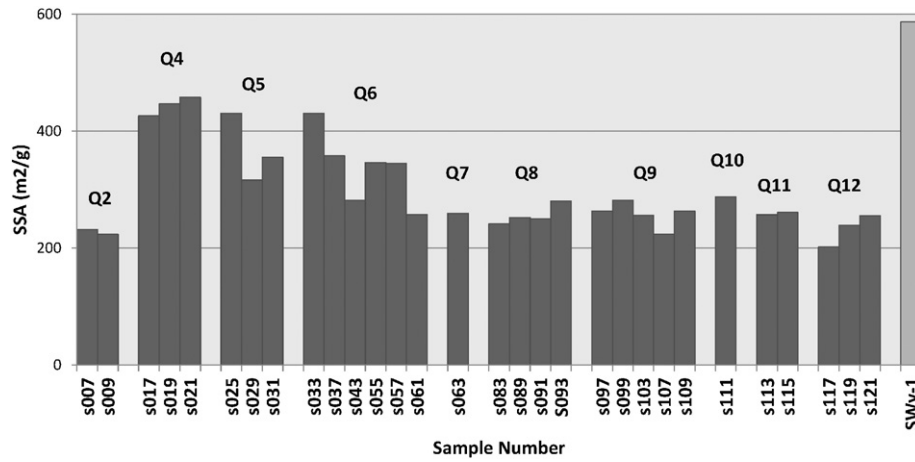


Fig. 1. Average specific surface area (SSA) for selected Egyptian bentonitic clays and the reference clay, SWy-1 (m^2/g). Q – quarry number.

only minor effect on DCS at the same water content. Incremental increases in water content more than doubled the DCS.

3.5. Rheological properties

All bentonitic clay slurries showed shear-thinning (pseudoplastic) properties. Viscosity values of untreated bentonitic clay slurries containing 3 wt.% clay varied from 0.25 to 1.2 cP at 600 rpm. Viscosity increased with decreasing shear rate (i.e. shear-thinning) and varied from 0.3 to

3.6 cP at 100 rpm. Viscosities for SWy-1 bentonite were 0.45 and 0.6 cP at 600 and 100 rpm, respectively. The plastic viscosity (Pv) and yield point (Yp) of the Egyptian samples ranged from 1 to 3.5 cP, and 0 to 6 lb/100 ft², respectively. The ratio of Yp/Pv varied between 0 and 3.

Viscosity values for SWy-1 were 2.9, 3.8, 4.5, and 7.2 cP at 600, 300, 200, and 100 rpm with 6 wt.% suspended bentonite. The majority of samples had viscosities below the reference bentonite for the same slurry concentration, except for three samples (s021, s111, and s119) that had higher values at the different rotational speeds (Fig. 3). Plastic

Table 4

Swelling test results for raw and Na-activated samples (ml gel/10 g dry sample). Shaded blocks indicate maximum swelling. (*) indicates halite-bearing samples.

Sample	Swelling index							
	Raw (ml gel/10g)	Swelling index after Na-activation (ml gel/10g)						Swelling capacity
		Na ₂ CO ₃ 1wt%	Na ₂ CO ₃ 2wt%	Na ₂ CO ₃ 3wt%	Na ₂ CO ₃ 4wt%	Na ₂ CO ₃ 5wt%	Na ₂ CO ₃ 6wt%	
s007*	53	65.9	71.2	68.3	66	63	64	134.30%
s021	49	110.2	149.6	169.7	150.8	151.7	150	346.20%
s029*	60	87	78	74	63	51	54	145.00%
s033	43	100	95	96	92	86	78	232.60%
s061	55	100	104	104	103	84	80	189.10%
s063	34	62	68	65	65	57	65	203.00%
s083	49	82	80	84.1	83.3	87.2	93.3	190.30%
s091	36	67	77	74	69	65	60	213.90%
s099	45	80	90	84	74	72	70	200.00%
s109	40	70	80	73.5	75	71	65	200.00%
s111	71	115.3	122.7	110.7	106	97	95	172.80%
s113*	44	55	55.5	54	53	50	47	126.10%
s119*	82	88.5	73	62	56.5	51.5	50	107.90%
Na-Wyoming	96							

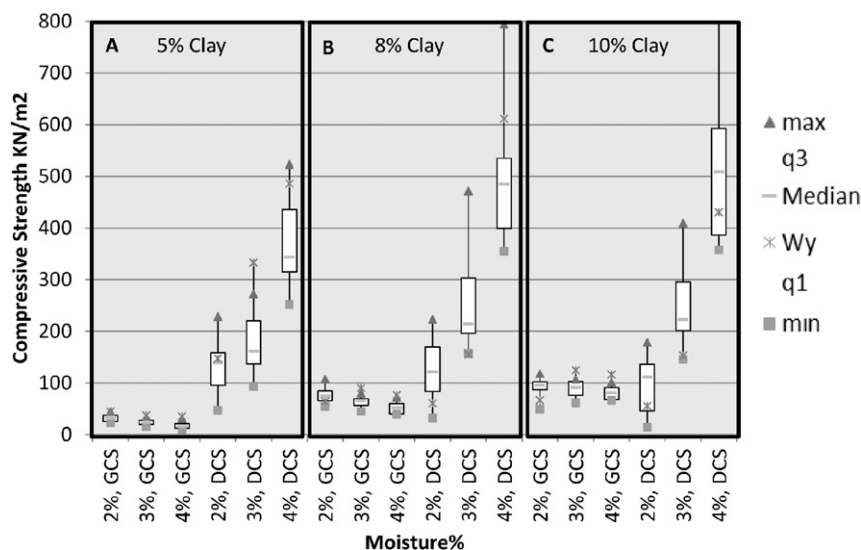


Fig. 2. Boxplot of summary statistics for the compressive strength results of the Egyptian bentonitic clays mixed in different proportions and water content with molding sand. Max – maximum value; min – minimum value; q1 and q3 – first and third quartiles; Wy – value for SWy-1.

viscosity ranged from 1.5 to 7.5 cP and the ratio of Yp/Pv varied between 0 and 5.5. Filtrate volume of the Egyptian samples varied between 22 ml and 50 ml. The SWy-1 filtrate volume was 11.5 ml.

Viscosity values increased at 8 wt.% raw bentonitic clay, and still exhibited shear-thinning properties. Viscosity varied between 0.35 and 14.6 cP at 600 rpm, and at 100 rpm ranged from 0.6 to 72 cP. Viscosities produced by SWy-1 were 12, 17.2, 23.4, and 42 cP at 600, 300, 200, and 100 rpm. Only one sample (s111) had better viscosity than the Wyoming bentonite. The rheological parameters, Pv and Yp, ranged from 1.5 to 14 cP, and 0.5 to 118 lb/100 ft², respectively. The ratio of Yp/Pv varied between 1.5 and 8.4.

After activating the bentonitic clays with the optimum percentages of Na₂CO₃, as determined by the swelling index test, the improvement percentage of rheological parameters at 6 wt.% suspension concentration ranged from about 50% to 400%, for s021, s061, s063, s083, s091, s099, and s109 (Fig. 4). The remaining samples (mainly halite-bearing) showed insignificant improvement or even negative percentages suggesting reduction in the rheological properties after activation. Similar results were obtained for the 8 wt.% suspension concentration. The filtrate volume improvement was insignificant in both cases. At

3 wt.% clay, the comparison of untreated and activated samples was very difficult due to the low viscosity values for both the raw and activated samples.

4. Discussion

4.1. Specific Surface Area (SSA)

Surface area and cation exchange capacity are two of the first properties to be determined in the assessment of bentonites and other clay types (Inglethorpe et al., 1993). They are frequently correlated with mineralogy and other physico-chemical characteristics of materials used in a variety of industrial applications. A simple bivariate exploration of the correlation of SSA with mineralogy, extractable (including exchangeable) cations, and AgTU-CEC revealed three associations with coefficients approximately equal to ± 0.7 (Fig. 5). The SSA was correlated (positively) with smectitic minerals content and AgTU-CEC. Kaolinites were inversely related to SSA. The other minerals with low exchange capacity had a very weak negative relationship to SSA. Direct comparison of the untreated bentonitic clay SSAs with SWy-1 revealed a

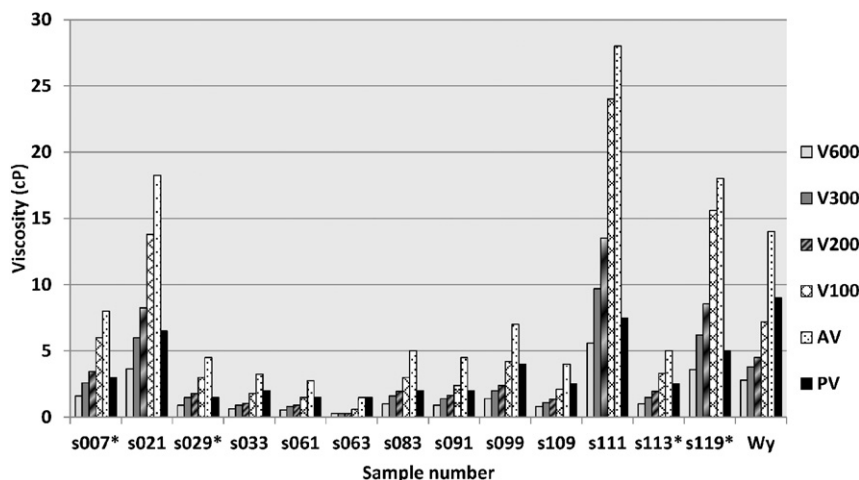


Fig. 3. Viscosity values for slurries of 6% suspended raw bentonitic clay. (*) indicates halite-bearing samples. V600 = viscosity at 600 rpm; V100 = viscosity at 100 rpm; AV = apparent viscosity; PV = plastic viscosity.

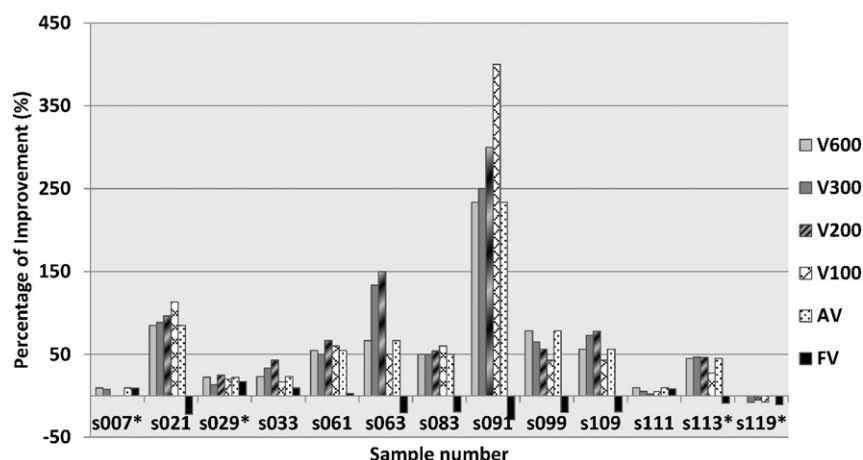


Fig. 4. Percentage of improvement after Na-activation for slurries of 6% suspended bentonitic clay. (*) indicates halite-bearing samples. Same legend as Fig. 3. FV = filtrate volume.

generally poorer quality material with values about 35–50% lower than the reference bentonite. Samples from quarry 4 had the highest SSAs; greater than 75% of SWy-1.

Further assessment of factors affecting the SSA data was carried out via multiple regression analysis. The equation contained five predictors: $SSA = -106 + (366 * aSmectites) + (-165 * aKaolinites) + (-164 * a[Qz + Feld]) + (118 * aK_{Ext}) + (118 * aMg_{Ext})$.

Each predictor is preceded by “a” to signify that the values used were isometric log transforms of the original XRD and extractable cation data. The model was characterized by a significant determination coefficient ($R^2 = 0.908$) indicating a strong relationship with the five independent variables. All the variables used in the regression were useful in predicting the measured value of SSA according to p-values and t-statistics at the 95% level of confidence. P-values for extractable Na and Ca were statistically insignificant which could be attributed to the presence of soluble minerals (halite and calcite) in some samples. Mineralogical and selected extractable cation values are a reliable predictor of SSA.

4.2. Swelling index and Na-activation

4.2.1. Swelling index of raw samples

Bentonites can be classified as swelling bentonite (Na-montmorillonite; swells 5 to 15 times its dry volume at full-unconfined saturation) and non-swelling (Ca and/or Mg-montmorillonite swells 2 to 5 times their original volume). The swelling bentonites show higher rheological and plastic properties, and higher degrees of dispersion when mixed with water than the non-swelling type (Inglethorpe et al., 1993). Thus, the swelling index test was a very important procedure to evaluate the possible performance of the bentonitic clay.

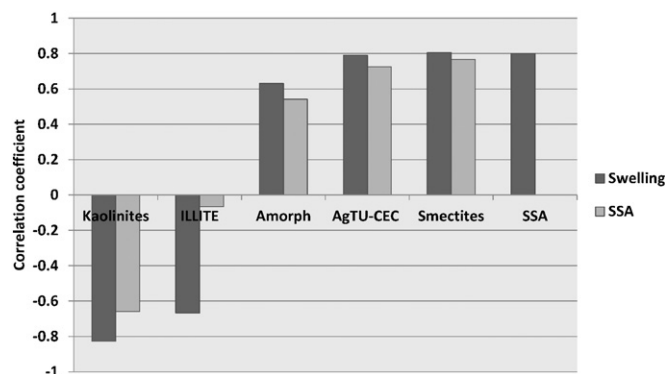


Fig. 5. Binary correlation coefficients relating mineralogical and exchange properties to SSA and swelling index after Na-activation.

Swelling index has been quoted frequently in civil engineering and drilling mud use specifications. For instance, a bentonite can be used to enhance greatly the performance of clay liners in engineered landfill sites when swelling index is ≥ 120 ml gel/10 g as specified by ASTM D5890-06 (2006). None of the Egyptian untreated bentonitic clays met this criterion.

For the untreated samples, the highest swelling index was reported for s119 (halite-bearing) that was relatively poor in expandable minerals (Table 4). Sample s021 (halite-free) was expected to have the maximum swelling index since it had more than twice the content of expandable minerals. It, however, showed a moderate swelling index (49 ml gel/10 g). Although s021 had the highest proportion of expandable minerals (about 70 wt.%) it swelled less than sample number s007 (halite-bearing) that had the lowest amount of expandable minerals. A statistical correlation analysis underscored the complexity of the factors influencing the swelling index as none of the chemical and mineralogical factors or SSA produced a significant correlation (absolute value of the correlation coefficient was approximately 0.5). This poorer correlation could be attributed to the presence of different types of smectite (i.e. Na- and Ca-types) and the presence of halite in some samples that caused a sort of Na-activation.

4.2.2. Swelling index of Na-activated samples and quality

The amount of soda ash required for ideal enhancement depends on the type of bentonite; about 2 wt.% for a mixed Na, Ca, Mg-montmorillonite to 5 wt.% for nearly pure Ca, Mg-type clays (Inglethorpe et al., 1993). Small percentages of Na_2CO_3 (1–2 wt.%) were required to activate the majority of the Egyptian samples suggesting the predominance of interlayer sodium over the other exchangeable

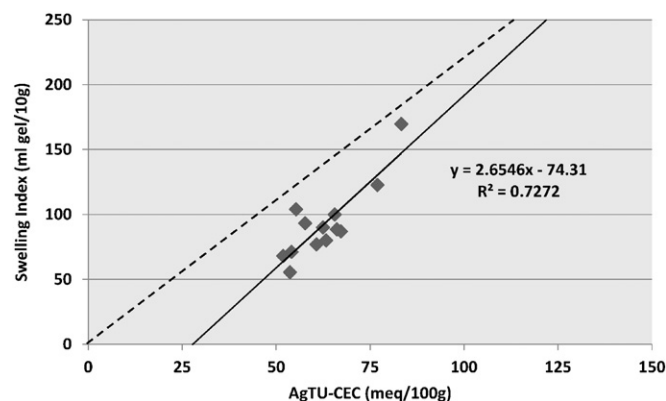


Fig. 6. SI of Na-activated samples related to AgTU-CEC. The dashed line corresponds to a theoretical regression line from Christidis (1998).

cations. The presence of halite was probably also a reason for the small percentages of Na_2CO_3 required for activation. The halite-bearing samples had a low swelling capacity, ranging between 108% and 145% (median = 130%); where the difference between the swelling indices before and after activation was small (Table 4). The highest swelling capacity was observed for the halite-free samples; ranging between 173% and 346% (median = 200%). Naturally occurring halite caused self-activation for some raw materials. Abundant halite facilitated the exchange of Mg and Ca by Na producing a higher swelling index for the initial raw samples.

4.2.3. Swelling index of Na-activated samples and grade

The correlation coefficients between the swelling index and the independent clay parameters increased in comparison to the SSA results (Fig. 5). Smectite, AgTU-CEC, and SSA were positively correlated with the swelling index, whereas kaolinites and illite were the highest negatively correlated variables. These significant relationships between swelling index and physiochemical characteristics suggested that swelling index of activated samples provided an indication of grade (smectite content). In addition, swelling index and CEC provided valuable information about impurities in bentonite. Christidis (1998) proposed a theoretical relationship between CEC and swelling index based on monomineralogic samples from the smectite zone of Kimolos Island, Greece. Deviation from the theoretical regression line (dashed line in Fig. 6) was reported to indicate the presence of non-swelling materials. The line ($R^2 = 0.72$) relating swelling index and AgTU-CEC for the Egyptian bentonitic clay samples deviated from the theoretical line (Fig. 6) confirming the possibility that non-swelling minerals produced the same effect in the Egyptian materials. The swelling index can be used to predict CEC with an accuracy of about 72%, where this percentage is comparable to the methylene blue method that accounts for 80% of true CEC values (Inglethorpe et al., 1993). The impact of mineralogy and CEC on swelling index was revealed by the following significant linear relationship ($R^2 = 0.96$):

$$\text{Swelling Index} = -459 + (25.5 * \text{aSmectites}) + (-72.5 * \text{allite}) + (305 * \text{aCEC}).$$

4.3. Compressive strength

Smectite and kaolinite are commonly used as bonding agents (in foundry sand, pelletizing, and ceramic industries) due to their plasticity when activated by water and strength upon drying. Ca-bentonites produced higher GCS and lower DCS than Na-types (Murray, 1999; Christidis, 2011). Kaolinite has been used also when excellent dry

or hot strength was required (Ammen, 1979). Thus, Na- and Ca-bentonites, and kaolin can be used separately or as blends to provide the satisfactory mold strength depending on the nature of casting metal, the size and geometry of the casting, and the equipment type (Inglethorpe et al., 1993; Tikalsky et al., 2004; Harvey and Lagaly, 2006; Murray, 2007; Ademoh, 2008; Eisenhour and Brown, 2009).

4.3.1. Effect of physiochemical properties

GCS and DCS of the Egyptian bentonitic clays were variable with respect to swelling index, SSA, mineralogy, and CEC. Samples with 4% water generally have higher values of the correlation coefficient with GCS that are greater than those with 2% water (Fig. 7). Correlation coefficients with an absolute value greater than 0.6 were statistically significant. The strongest GCS positive correlations were with swelling index, SSA, and AgTU-CEC. Although not as strong, there was a correlation of GCS with mineralogy; positive with smectite and negative with kaolinite. In contrast, DCS was negatively correlated with SSA, swelling index, CECs, and smectite; and positively with kaolinites. The associations for DCS may not be statistically significant. The impact of kaolinite on compressive strength could be a significant reason for the relatively high DCS values of the Egyptian samples, and the high GCSs of the Wyoming bentonite. Similarly, the relationship between compressive strength and mineralogy may explain why smectite-rich samples (e.g. s021) exhibited relatively higher GCS, but lower DCS than the kaolinite-rich samples (e.g. s007).

4.3.2. Effect of water and clay

There was a contrasting behavior of GCS and DCS with water content. The GCS values decreased slightly with increasing quantities of added water, at a given clay percentage (Fig. 2A, for instance). For DCS, the values obviously increased as the amount of added water increased from 2 wt.% to 4 wt.%. Similarly, there was a contrasting behavior of GCS and DCS with clay content, at low moisture content. At given water content, the GCS coefficients increased as the clay amount increased (Fig. 2). The behavior of DCS was variable. At 2 wt.% moisture, the DCS values slightly decreased as the bonding clay percentage increased. At higher moisture contents the DCS values increased as the clay increased from 5 wt.% to 10 wt.%. Increasing the water content resulted in improving DCS, while GCS was higher with more clay.

4.3.3. Suitability for foundry purposes

The satisfactory range of GCS and DCS values for castings used for various ferrous and nonferrous metals and alloys according to Dietert (1966) vary with anticipated product. The minimum satisfactory compressive strength values for gray and malleable iron casting are: GCS = 45 kN/m²; and DCS = 200 kN/m². The contrasting relationship between GCS and DCS, with respect to moisture content, made selecting

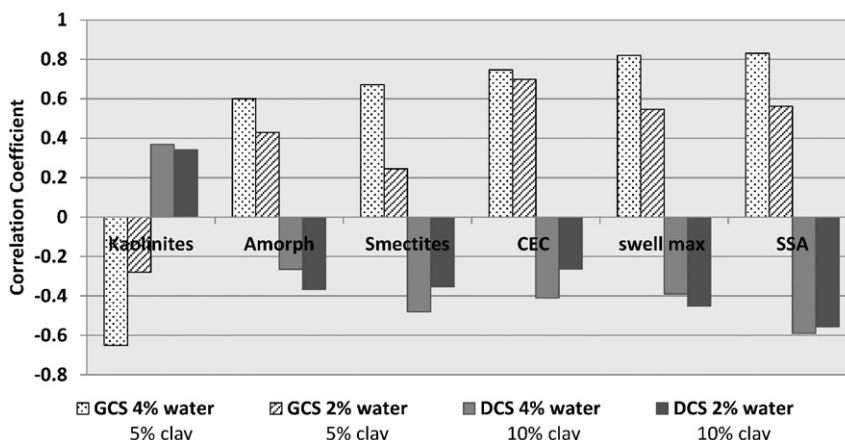


Fig. 7. Binary correlation coefficients for compressive strength and physiochemical properties of the Egyptian samples at different percentages of water and clay content.

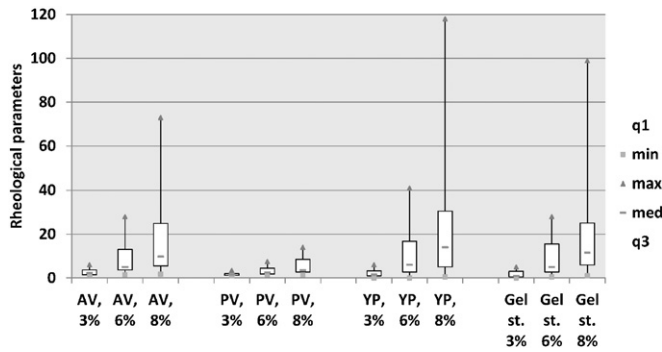


Fig. 8. Summary statistics of rheological parameters with varying clay wt.%. AV = apparent viscosity (cP); PV = plastic viscosity (cP); YP = yield point (lb/100 ft²); Gel st. = 10 s gel strength (lb/100 ft²).

the suitable mold mixture ratio for casting purposes a difficult task. At 5 wt.% clay, the DCS of mixtures composed of 5 wt.% clay and 4 wt.% water ranged between 252.3 and 523 kN/m², suitable for most casting purposes. However, none of the molded samples had GCS value ≥ 45 kN/m² at any moisture percent. Thus, the Egyptian clays were not suitable for use in common foundry applications at 5 wt.% bonding clay.

The majority of the sand molds bonded by 8 wt.% clay with 3 wt.% water produced GCSs and DCSs suitable for molding light metals such as aluminum, brass, bronze, and light gray iron (Fig. 2B). The minimum satisfactory compressive strength values for steel and high-duty iron castings gray and malleable iron casting are: GCS = 70 kN/m²; and DCS = 350 kN/m²; attainable with mixtures containing 10 wt.% clay and 4 wt.% water (Fig. 2C).

4.4. Rheological properties

4.4.1. Effect of clay concentration and mineralogy

The rheological parameters of the Egyptian raw bentonitic clays (apparent viscosity, plastic viscosity, yield point, and gel strength) were generally increased or improved by increasing the bentonitic clay amount from 3 wt.% to 8 wt.% (Fig. 8). Viscosity increased with increasing clay proportions as a result of the diffuse ionic layers around the clay particles confining the motion of these particles (Lagaly, 2005, 2006). However, the proportion of rheological improvement among the Egyptian samples was not similar to SWy-1. The viscosities of the Egyptian clays were comparable to the reference material for low suspension concentrations (3 wt.% clay), except for three samples (s021, s111, s119) that had higher values. These three samples and the standard bentonite exhibited a marked increase in their rheological

parameters with clay concentration; i.e. possible use as high-yield drilling clays.

Most rheological parameters showed positive correlations with the measured AgTU-CEC and maximum swelling index, and were negatively correlated with abundance of quartz plus feldspar (Fig. 9). The filtrate volume varied directly with increasing quartz plus feldspar. Samples s021 and s111 contained the highest AgTU-CEC and smectite content, and the lowest quantities of kaolinite. The high grade of s021 and s111 was in harmony with their better rheological properties. Surprisingly, s119 showed rheological properties comparable to the Wyoming bentonite at the different suspension concentrations, although it had lower smectite content and a relatively moderate AgTU-CEC value. Such poor to moderate grade material did not produce moderate rheological properties as expected. This indicated that other controlling factors beyond grade, such as swelling index were involved. The halite-bearing s119 exhibited the highest swelling index among the raw samples (Table 4). This behavior and its high viscosity could be due to the presence of halite with colloidal iron oxides revealed by SEM. The sharp increase in rheological parameters occurred due to self-activation by halite. In addition, abundance of halite could develop aggregation in the form of networks that confine the translational and rotational motion of smectite particles (Lagaly, 2005, 2006). The presence of iron oxide particles can bridge the negative clay particles (either smectite or kaolinite) and develop a strong physical network of attractive clay-iron oxide particles, increasing the viscosity markedly (Yong and Ohtsubo, 1987; Baird and Walz, 2006; Lagaly, 2006; Lee et al., 2009; Jung et al., 2011).

4.4.2. Activation

The impact of activation on rheological parameters was variable with respect to clay/water ratio. Some bentonitic clays exhibited improvement in viscosities, while others deteriorated. The percentage of improvement was generally insignificant for the low clay/water ratio, and notably increased with increasing suspension concentration. Na-activation improved the rheological properties for halite-free samples (Fig. 4). On the other hand, the halite-bearing samples showed an insignificant improvement or even reduction in rheological parameters with increasing clay/water content. The impact of activation on the rheological parameters behavior was more or less similar to swelling index behavior, regarding the presence of halite.

The question now is; can the swelling index be used as an indication for high-yield drilling clays? The Na-activated s021, s033, s061, and s111 samples exhibited the highest swelling indexes, even higher than SWy-1. The apparent viscosity was relatively high for the smectite-rich s021 and s111 only; where their viscosity values exceeded the reference bentonite, while s033 and s061 produced very low viscosities.

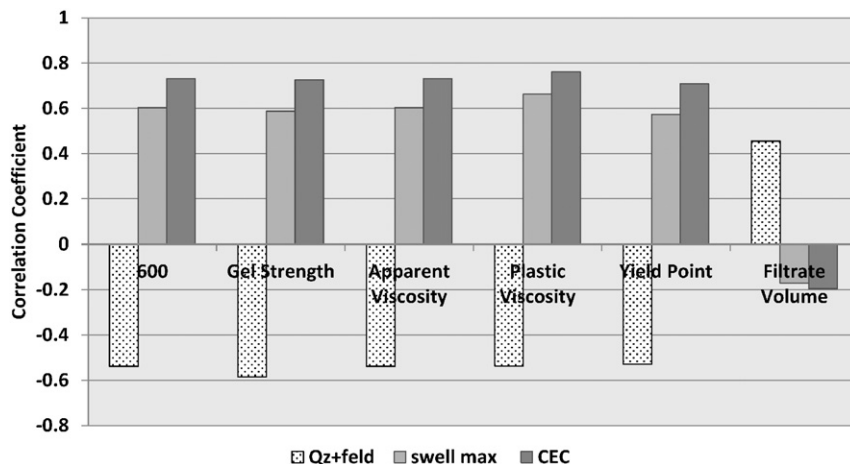


Fig. 9. Binary correlation coefficients of rheological parameters against selected rock properties at 6 wt.% clay. 600 = viscosity in cP at 600 rpm.

The low-viscosity samples with high swelling index, contained abundant quartz and feldspar (7 wt.% and 15 wt.%, respectively), while s021 and s111 contained scarce quartz and feldspar (about 3 wt.%). Thus, viscosity depended on swelling index, but abundant quartz and feldspar reduced it.

4.4.3. API and OCMA specifications

Assessment of the Egyptian bentonitic clays suitability for drilling mud, rheological and filtration properties of the bentonite slurry should comply with international standard requirements such as API or European Oil Companies Materials Association (OCMA) specified values. The viscometer dial reading at 600 rpm of the high-yield drilling raw samples (s021, s111, and s119) was >3 cP, thus meeting the API and OCMA standards, at clay concentration of 6 wt.%. The SWy-1 dial reading was 2.9 cP under the same conditions. Two additional samples (s091 and s099) produced dial readings at 600 rpm ≥ 3 cP, when Na-activated or when the suspension concentration was increased to 8 wt.%.

Only the samples that recorded ≥ 3 cP at 600 rpm (or potential high-yield raw or activated drilling clays) will be discussed. The yield point/plastic viscosity ratios for s021, s111, and s119 were <6 and met the OCMA standard for the 6 wt.% clay. At the clay concentration of 6 wt.% and 8 wt.%, the SWy-1, s091, and s099 raw samples had yield point/plastic viscosity <3 dictated by the API standard. Na-activation slightly reduced the yield point/plastic viscosity of s111 and s119, and increased it for s021, s091, and s099.

The Egyptian bentonitic clays did not meet the international standards related to filtrate volume. Only SWy-1 produced filtrate volumes less than 15 ml (the API recommended filtrate volume). The filtrate volume was dependent on quartz and feldspars proportions. The filtrate volume can be reduced by minimizing the proportions of quartz and feldspars (by physical separation technique) or by treating the Egyptian bentonitic clays with an additive such as starch and CaCO_3 (Toka and Toka, 2015).

5. Conclusion

The assessment of selected Egyptian bentonitic clays in the NWD demonstrated the significant impact of mineralogy and CEC on their physical properties. More than 90% of the SSA variations were accounted by smectites, kaolinites, quartz, feldspars, and extractable K and Mg. More than 95% of the swelling index variations for the activated samples were related to changes in smectite, illite, and AgTU-CEC. The relationship between swelling index of raw samples and the physiochemical independent variables was insignificant due to: 1- variable smectite type (Na/Ca) greatly influenced the swelling index, and 2- presence of halite resulted in self-Na activation with some improvement in the swelling index. The natural blend of the Egyptian bentonitic clays containing variable ratios of smectite to kaolinite resulted in superior GCS due to the prevalence of smectite. The DCS was adversely affected by higher smectite quantities. Furthermore, GCS increased with increasing clay amount, while DCS increased with the moisture content. The rheological properties of the Egyptian bentonitic clays were correlated positively with AgTU-CEC and SI. The easily determined SI test, after Na-activation, can be used as preliminary check to assess grade, presence of non-swelling minerals, AgTU-CEC, compressive strength, and rheological properties.

The presence of minerals other than smectite had effects on physical properties. Halite, through self-activation, and colloidal iron oxides in some samples may have improved the SI and rheological properties. Quartz and feldspars reduced the rheological properties and increased the filtrate volume. Na-activation identified the optimum percent of Na_2CO_3 that improved swelling index and viscosities for halite-free samples.

The comparison between Egyptian bentonitic clays and the high-grade Wyoming Na-bentonite (SWy-1) revealed that SSA and swelling

index values for SWy-1 were always higher than the Egyptian raw-samples. Two samples (s021;Q4 and s111;Q10) frequently showed comparable, or even higher, values than SWy-1 for swelling index (after activation), rheological properties and GCS. These two samples deserve further evaluation. Most of the Egyptian samples showed higher DCSs than SWy-1, due to the presence of kaolinite.

Regarding industrial applications; bonding sands with 8 wt.% Egyptian bentonitic clays at 3 wt.% moisture content are suitable for casting light iron sections and nonferrous metals. For steel and heavy iron sections, a mold mixture composed of 10 wt.% Egyptian clays and 4 wt.% water would be required. Five Egyptian samples (s021,Q4; s111,Q10; s119,Q12; s091,Q8; and s099,Q9) had rheological properties that met the international standards for drilling mud. The first three samples can be used as drilling mud at 6 wt.% suspension concentration without Na-activation. However, the Egyptian bentonitic clays may still require an additive to reduce the filtrate volume loss. Samples from Q4 were identified previously as having characteristics most typical of bentonites formed from direct alteration of volcanic deposits. More than half of the deposits cannot be considered commercial bentonitic clays because of their generally poor behavior during the assessment tests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.clay.2015.08.016>.

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